



by Jim McKinley

Permeation Tubes: A Pragmatist's Approach to Creating Almost Nothing

Permeation tubes offer the “path of least resistance” to traceability.

The production of trace concentration calibration gas mixtures is a challenging process that faces increasing requirements, especially for the calibration of newer, sophisticated analytical instruments. The permeation tube is a molecular-based flow control device that is ideally suited for that purpose.

While lower and lower concentrations of an increasing number of complex compounds are required, confinement as stable, static mixtures remains a problem for trace concentration mixtures.

Examples include mixtures at extremely low concentrations (ppb, ppt, even ppq); mixtures of aggressive compounds (HCl, HF, etc.); mixtures of “chewing gum” molecules, such as SO₂ and most amines; and mixtures of compounds that spontaneously change, or react slowly, such as formaldehyde, SO₂ + H₂S and NO + O₂. Add to the list mixtures that contain trace levels of atmospheric constituents—that the entire world seems to oppose.

Creating mixtures for these applications typically means giving up on the revered static mixture in a cylinder and dynamically blending the mixture.

However, there are also significant problems in dynamically blending mixtures—particularly trace concentration mixtures. The most significant is: How is the flow of the trace component measured and controlled?

A typical setup that uses thermal mass flow meters to blend a one ppm mixture in a single step requires 0.1 cc/min of

analyte vapor be added to 100 l/min of dilution gas. A greater challenge is finding a reliable 0.1 cc/min flow controller and then accurately calibrating it for the trace component compound. Of equal concern is obtaining a source of vapor flow.

Where can a 0.1 cc/min flow of p-xylene vapor be obtained? Or, better still, phenol vapor? Once these questions are resolved, there is still the challenge to certify the accuracy of the resulting mixture.

Mechanical solutions to many of the problems exist; however, the point is that yesterday's methods are not well adapted to many of today's problems. Creating and supplying accurately known trace concentration mixtures is not a trivial problem.

Permeation tubes are a frequently overlooked method for solving, or avoiding, most of the problems associated with dynamically blending trace concentration gas mixtures.

The Seventh Simple Machine

Permeation tubes were first described by Andrew O'Keefe and Gordon Ortman in 1966. They were attempting to create primary standards for ambient air monitoring, primarily for SO₂ and NO₂.

The major challenge in creating dynamically blended mixtures is the control and measurement of extremely small flow rates over a wide range of analyte vapors.

Figure 1 illustrates a basic, disposable permeation tube. Liquid analyte (the trace concentration component) is sealed

inside a length of plastic tubing. The tubing wall is a permeation membrane that permits analyte vapor to pass through the tubing wall and escape to the atmosphere surrounding the tube. The flow of escaping vapor is very small and is usually expressed in nanograms/minute. When the tube is held at constant temperature, the emission rate is very stable. The flow rate of analyte emitting from the tube is measured gravimetrically by periodically weighing the tube while it is held at constant temperature in a flow of dilution gas. Teflon (either TFE or FEP) tubing is usually selected because it is inert and possesses favorable mechanical properties.

Trace concentration mixtures are created by immersing the tube in a flow of dilution gas as shown in Figure 2.

Disposable permeation tubes of the type depicted in Figure 1 can typically be designed to have emission rates in the range from approximately 20 nanograms/minute to approximately 5,000 nanograms/minute.

The practical limit at the low emission end is determined by the ability to ac-

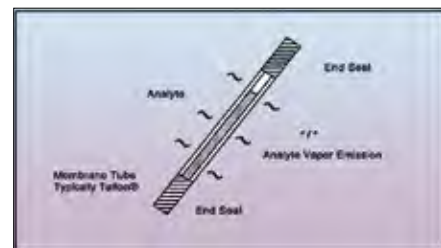


Figure 1. Trace concentration mixtures are created by immersing the permeation tube in a flow of dilution gas.

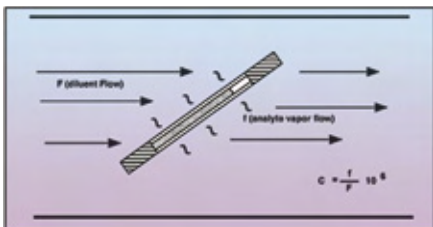


Figure 2. Using permeation tubes.

curately measure the rate of weight loss from the permeation tube within a reasonable period of time. At 20 ng/min, for example, that period can be 35 days between weights to achieve a plus or minus one percent weight-loss accuracy using a semi-micro analytical balance.

The high end of the flow scale is set by the useful life that can be obtained from a tube. At 5000 ng/min, a tube that contains 0.5 gm of analyte compound will have a useful life of approximately 60 days of continuous service. This emission rate range yields concentrations ranging from less than 5 ppb in 5,000 cc/min for 20 ng/min to more than 10 ppm for a 5,000 ng/min tube with 250 cc/min dilution flow.

Other tube designs permit much higher emission rates and operating life spans.

Where Permeation Tubes Really Shine

While trace concentration mixtures can be generated by a variety of methods, there are four types of applications in which the permeation tube method excels:

1. Producing and delivering extremely low concentrations, particularly in the ppb, ppt, and ppq regions.
2. Achieving traceability to NIST.
3. Making "complex" mixtures.
4. Providing a continuous, long-term flow of trace concentration test gas.

For Really Low Concentrations

The advantage of the permeation tube method to achieve extremely accurate trace concentrations is achieved through the large single-step dilution ratio. With permeation tubes, a dilution ratio of $10^6:1$ is very simple, and a ratio of $10^8:1$ is quite practical. That yields concentrations of 10 ppb and less with single-step dilution directly from the pure analyte compound. Adding a second dilution step of 1000:1 reduces the concentration to the low ppt region, and a third step would produce concentrations down to the low ppq.

Another method that can be used with some analytes is to conduct sequential dilutions, using two permeation tubes in series. That technique can produce a dilution ratio of $10^{16}:1$ with only two steps of dilution.

Establishing the blank, or "zero" concentration is an additional concern at extremely low concentrations. Often "zero" simply does not exist. Using the "method of standard additions" is an effective way to deal with this situation.

The partial pressure of analyte vapor in the mixture is very low compared to the vapor pressure of the pure analyte. As a result, the emission rate of a permeation tube is essentially independent

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of the background concentration in the dilution gas. This makes permeation tubes ideally suited as “standard addition” sources. The calibration of an analyzer can be based on the change in response caused by adding the permeate flow, thus eliminating, or at least minimizing, the effect of background contamination on calibration accuracy.

Achieving Traceability

The International Vocabulary of Basic and General Terms in Metrology (VIM) defines traceability as “[The] property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties.”

While this definition is simple, actually achieving traceability of a trace concentration gas standard is not so straightforward. Under the VIM definition, the clearest path to traceability is comparison to a primary standard, such

as a standard reference material (SRM) from the National Institute of Standards and Technology (NIST), or to a secondary standard, such as a National Technical Reference Material (NTRM).

The problem is that very few such standards are available.

For trace concentration gas analysis, SRMs are available at some level for approximately 35 compounds (primarily supplied as static mixtures) for only one concentration level, and in a nitrogen matrix. There are, however, well over 400 analytes in a variety of matrices and over a large range of trace concentrations that are of current industrial and environmental interest.

Where no applicable SRM is available, an alternate path to traceability is directly through physical standards. If the concentration of a mixture can be related to physical variables (mass, length, time, etc.) for which standards exist, then traceability of the measured values of those variables gives traceabil-

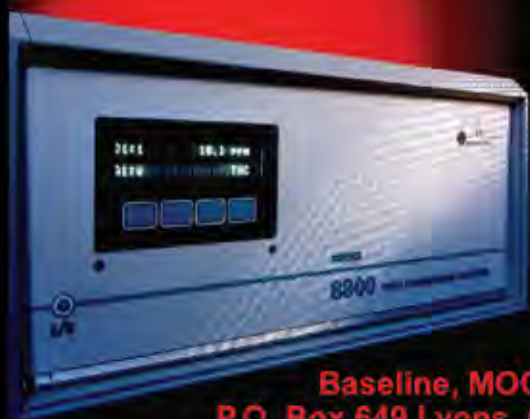
ity of the resulting concentration.

Static mixtures are unquestionably the most user friendly form of gas standard. Their preparation procedures are straightforward and the controlling variables (primarily mass measurements) can be readily traced to NIST. The question is: “Is the mixture stable?”

The gases themselves can react, and the container itself can change the mixture. Both of these considerations introduce undefined errors that destroy the value of traceability of the preparation process. In short, you can know what you put in the mixture, but you don’t know what you are getting out. Static mixtures are traceable only through comparison to other traceable concentration standards.

Considering the aggressive properties of many analyte compounds, permeation tubes offer the “path of least resistance” to traceability. The strength in the permeation tube approach is that the undefined error sources are avoided. When a

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known concentration is created through traceable measurement and control of fundamental variables, and used immediately, then the unknown error sources of instability and container effects are avoided, and the mixture is still traceable when it is used.

For Complex Mixtures

Mixtures are complex when there are factors that make storage impossible, or at least totally impractical. An example is mixtures in which the components react slowly, either with each other or with the matrix. The components, of course, must be added to the matrix in parallel. Permeation tubes, where a membrane isolates the neat analyte from surrounding gases, offer the simple, parallel addition method for combining reacting components. Since the mixture is used immediately, the effects of component reactions are minimized.

Another complex situation occurs in humidified mixtures. In general, humidity must be the last addition to a mixture. Again, the membrane separating the pure analyte from the mixture is useful in isolating the analyte compound from contamination by water vapor back streaming in the system.

Other problem mixtures may contain higher concentrations of solvents that have a higher boiling point, e.g. a mixture of xylenes at over 1,000 ppm. Generally, mixtures containing any semi-volatile compounds with a high boiling point. Using special, high capacity tubes that operate at elevated temperature allows on-demand preparation of mixtures near the saturation point.

Long-term, Continuous Source of Test Gas

Typical applications that require this type of gas source include:

- Filter evaluation and capacity testing.
- Mixed flowing gas corrosion rate testing.
- Defining the effects of various impurities on catalyst systems.

Permeation tubes are an ideal system for these applications. Since the tubes emit continuously, the primary operating cost is the cost of the matrix (dilution) gas.

Changing the concentration of the test gas requires only a change in the dilution ratio or operating conditions for the permeation tube. Conversely, cylinder gas mixtures, when available, are expensive, require frequent attendance, and are the primary operating expense in such testing.

How Permeation Tubes Work

The permeability of a compound through a membrane is defined as the product of the solubility of the compound in the membrane and the diffusivity of the compound through the membrane.

$$K(T) = D * S \quad (\text{Equation 1.})$$

Where:

K(T) is the permeability of the analyte through them membrane as a function of temperature

D is the diffusivity of the analyte through the membrane

S is the solubility of the analyte in the membrane

Both the diffusivity and solubility are functions of temperature. It is important to note the solubility portion in Equation 1. When the temperature changes, the actual permeation rate will change slowly, while the amount of analyte dissolved in the membrane re-equilibrates due to the change in solubility with temperature.

The flow rate of analyte vapor from a permeation tube is given by:

$$f = K(T) (A \Delta P/t) \quad (\text{Equation 2})$$

Where:

f is the flow rate of analyte emitted by the tube

K(T) = the permeability of the membrane to the analyte at temperature "T."

A = the membrane area over which permeation occurs.

ΔP is the difference in partial pressure of analyte vapor across the membrane.

t = the membrane thickness.

In Equation 2, the term **ΔP** is of particular interest. For a tube containing liquid

analyte, ΔP is actually the vapor pressure of the analyte, and is therefore a function of temperature. Also, this means that the emission rate does not change until all of the analyte liquid is consumed, or some other factor causes a change in vapor pressure of the analyte liquid (polymer formation, for example).

Permeation tubes also function effectively when only the vapor phase of the analyte contacts the membrane, provided that the partial pressure of the analyte gas is constant. Thus, permeation tubes can also be used to dilute permanent gases, such as oxygen, hydrogen, and ethylene.

Finally, Equation 2 shows that the emission rate depends on the difference in analyte partial pressure across the membrane—not the total pressure. Thus, permeation tubes can be used to create pressurized mixtures, or mixtures under vacuum, so long as the pressure does not disrupt the mechanical integrity of the device.

The permeability function $K(T)$ varies exponentially with absolute temperature.

$$K(T) = \beta e^{-\alpha/T} \quad (\text{Equation 3})$$

Where:

α , β are constants

T is the absolute temperature in degrees Kelvin

With dependence on two exponential variables, the flow of analyte from a permeation tube clearly depends strongly on temperature. The emission rate approximately doubles with a 10 C change in temperature.

In 1966, when permeation tubes were introduced, temperature control to plus or minus 0.1 C (i.e., about plus or minus one percent change in emission rate) was a significant problem. Early on, workers struggling to achieve adequate temperature control were often frustrated, and permeation tubes were somewhat burdened with the reputation of being “hard to use.” With modern electronics, achieving plus or minus 0.1 C temperature control is no longer a problem.

Using Permeation Tubes Effectively

Three special characteristics must be considered when using permeation tubes to blend a gas standard:

- Permeation tubes are equilibrium devices,
- Their emission is continuous, and
- The mixtures created are dynamic.

Equilibrium Devices—During start-up, when temperature and operating pressure are changing, solubility effects can lead to unexpected transient emission rates from the tube. If for example, the solubility of analyte in the membrane is higher at the operating temperature than at the storage temperature, then the emission may initially be quite low and rise only slowly. Conversely, if the solubility is lower at the operating temperature, the emission rate may be quite high as the tube ‘dumps’ the excess dissolved analyte. Once equilibrated, the emission becomes very stable. Systems using permeation tubes should be designed to take advantage of this property. One would not, for example, normally use temperature programming to generate a range of concentrations. Generally speaking, it is good practice to allow at least 12 hours for a tube to equilibrate at a new operating temperature.

Emission is Continuous—Permeation tubes emit continuously. When the dilution flow is stopped, the concentration in the system begins to rise. The significance of this rise is not well recognized. For example, a system with 150 cc internal volume is producing 400 ppb of analyte in one liter/min dilution flow. If that dilution flow is blocked for one minute the concentration will rise more than sixfold to 2.6 ppm. If the internal volume was only 15 cc, the concentration, after one minute, would be more than 25 ppm. A concentration shift of this size can easily make it necessary to re-equilibrate at the desired 400 ppb level.

Mixtures are Dynamic—One desirable

feature of a static mixture in a cylinder is that the concentration is what it is—right or wrong. The user does not normally have control of that concentration. With a dynamic mixture, the user is in control and has the ultimate responsibility for the accuracy of the mixture.

The accuracy and precision of a permeation tube mixture depend on the accuracy and precision of the dynamic variables, such as temperature and dilution flow, used to create the mixture. As a rule-of-thumb, a temperature change of 0.1C causes a one percent change in emission rate. Similarly, a one percent change in dilution flow would result in approximately a one percent change in concentration. It also follows that a one percent error in the measured emission rate will cause a one percent concentration error.

Thus, a permeation based mixture can have an error band of less than plus or minus two percent—truly exceptional for ppb mixtures of reactive gases. Using exceptional temperature and flow controls can limit the error band plus or minus one percent or less.

However, if the temperature is maintained at just plus or minus 0.5 C, and a plus or minus five percent flow meter is used for dilution flow measurement, the accuracy that can be expected is plus or minus seven percent—even if the permeation tube is certified to plus or minus one percent. The quality of the mixture is user controlled.

Using the Mixture—Think Flowing Gas!

The use of a permeation system analyzer calibration requires a change in the thought process; i.e., a paradigm shift. Calibration is an on-off process when a conventional cylinder gas is used as the span gas. That can be compared to drawing a bucket of water from a tank, and saving the rest for future needs. Permeation tubes, however, produce a flowing stream. When the required portion is drawn to fill an immediate need, the remainder continues to flow. Most application errors

stem from failing to recognize this simple difference.

The total gas volume from the permeation system is chosen to produce a desired concentration from a specific permeation tube. Flow to the analyzer, on the other hand, should remain constant, regardless of the concentration.

Figure 3 shows a block diagram of a best-practice interface to an analyzer. Gas from the permeation system flows through a manifold to vent—either through a back pressure controlling relief valve, or directly to the atmosphere. A side stream flows from the manifold to the analyzer. Flow to the analyzer is usually controlled by the analyzer's internal sample flow controls.

This scheme effectively converts the flow-controlled mixture from the permeation system to a pressure regulated source in the manifold. Changing dilution flow to change the mixture concentration has no effect on the flow to the analyzer. **SGR**

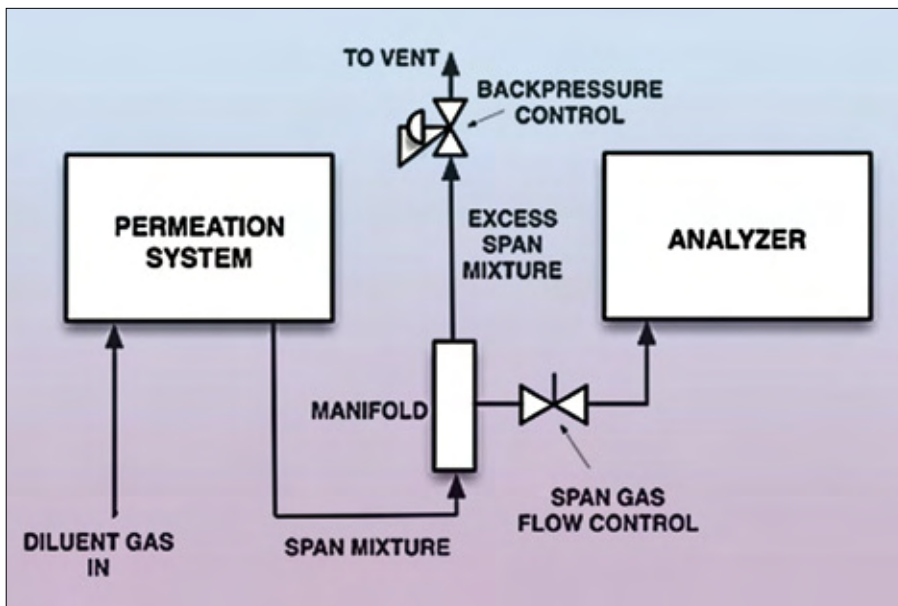


Figure 3. Block diagram of a best-practice interface to an analyzer.

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